Electronic structure calculation of AlN, $AlGaN_2$ and GaN in the wurtzite structure

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Band gaps and quasiparticle(QP) energies of AlN, $AlGaN_2$ and GaN in the wurtzite structure have been calculated by first principle within the GW approximation[1-5]. The linear muffin tin orbital(LMTO) basis[6] is used and d orbital can be treated as a valence state explicitly. The calculated quasiparticle band gaps are in good agreement with the experimental band gaps of AlN and GaN. That of $AlGaN_2$ has been predicted by first principles. We demonstrate the GW method is promising for a semiconductor device design technology by first principles at this conference.

Up to now, most works on ab initio device design have been based on the density functional theory (DFT)[7,8] within the local density approximation (LDA)[7,8]. They are intended to describe the material structure rather than the optical properties since the conventional DFT scheme cannot describe excited states in principle except for the highest occupied state. It is actually well known that the DFT-LDA calculation yields too smaller band gap than the experiments.

This failure is considered to originate from the self-interaction for the occupied states, the lack of the wavefunction dependency, the non-locality and the energy dependence in the exchange-correlation potential in the conventional DFT-LDA scheme. An occupied state should feel the potential generated by the N-1 electrons and an unoccupied state should feel that by N electrons, however, the conventional DFT-LDA does not distinguish this difference, which is a dominant origin of gap problems in the localized state. Moreover, the actual system has inhomogeneous distribution of the charge density but the LDA is based on the homogeneous electron gas.

Fortunately, there exits a more realistic but relatively simple way to describe the excitation states. It is known as the GW approximation (GWA), which has been developed since the early 1960s and can take into account both non-locality and dynamic (i.e. energy dependent) feature of correlation in many-body system. This approximation was originally derived from a many-body perturbation theory based on Green's function. The physical interpretation of the Green's function corresponds to the photoemission or inverse photoemission experiment. In short, the GWA can describe the dynamical phenomenon that an electron is added to or subtracted from an N-electron system with dynamical correlation, predict excited states of (N+1) or (N-1) electron system.

The computational flow is as follows; (1) The standard LMTO method within the atomic sphere approximation(ASA), which can be applied to systems with d and f electrons, is used to obtain the LDA eigen values and wavefunctions which are employed as input for the GW calculations. (2) The dielectric function is computed with the Green function which is constructed from the LDA eigen energies and functions. (3) The screened potential is calculated within the random phase approximation(RPA)[1,2] using the dielectric function. (4) The self-energy is obtained by the convolution of the Green's function and the screened potential. (5) The LDA eigen energy is corrected by the obtained self-energy and then the QP energy levels are obtained. The self-interaction problem in the LDA is removed and the many-body exchange and relatively long-range correlation corrections are taken into account by this nonlocal, energy-dependent and non-Hermitian self-energy operator.

We utilized some parallel computational technique in obtaining the screened potential. The machine that

is used for this work is the NEC SX-5 vector super-computer.

The experimental lattice constants are used for the AlN and GaN for more meaningful comparison with experimental data and theoretical results from literature, however, the lattice constant for $AlGaN_2$ was predicted by DFT-LDA and the QP energy levels of $AlGaN_2$ was obtained with this theoretically predicted lattice constant. The wurtzite lattice has four sub-lattices(i.e. the unit cell has four atoms). The experimental constant of a is 3.11 and 3.19 angstroms for AlN and GaN. The predicted a for $AlGaN_2$ is 3.13 angstroms. Here we suppose the ratio of c/a = square root (8/3) and the u = 0.375, which means the ideal wurtzite structure condition.

The obtained QP band gaps at the gamma point of AlN, $GaAlN_2$ and GaN are 6.5 eV, 4.7 eV and 3.4 eV, respectively. On the other hand, the conventional LDA band gaps are 4.6 eV, 3.1eV and 1.9 eV, respectively. The experimental gaps of AlN and GaN are 6.2 eV and 3.5 eV, respectively[9]. The QP band gaps are in good agreement with the experiment. It is interesting that the lattice constant of $AlGaN_2$ is closer to that of AlN but the band gap is closer to that of GaN. Experimental conformation is expected for $AlGaN_2$ result.

We also find the interesting feature about the location of the valence top which means ionization potential(IP) of the nitride systems in comparing with the wide gap II(Zn)-VI(O, S, Se) semiconductors[10,11]. The IP levels of the nitride system are higher than those of II(Zn)-VI(O, S, Se) by 1 or 2 eV. The relative location of these levels would be important for the photo chemical stability. The physical meaning of the IP is the highest excited state of N-1 electrons. Similar situation would occur in the semiconductor laser that is emitting and storing strong light. The hole is created by itself. Since the hole attracts the electrons from the material that is in contact with or adsorbed to the system, the ability of attracting electrons or photo chemical reaction activity would increase if the IP were located at a lower level. In some cases, this might cause a serious self-decay problem on the optical devices. Indeed, it is reported that the life time of the blue laser based on the Zn(S/Se) related system was much shorter than that on (Ga/In)N. The nitride luminescent device has been already developed for commercially practical use but the sulfide or selenide one has not yet been done. However, instead, we could regards this feature of photo chemical activity as a useful property for application to a sort of photo chemical catalyst.

The computational time to obtain the self-energy for AlN, for instance, was about 4 hours with one CPU of NEC SX-5. Our code has not yet been optimized, then some more improvement is expected.

Conclusion:

We have applied the LMTO-ASA-GW to the nitride wide gap materials. The obtained band gaps are in good agreement with experiment. The electronic structure of $AlGa N_2$ has been predicted by first principles. The computational time is moderate. We believe that this method would be a promising modern approach for the optical devise design technology. Since this method can obtain correct ionization potential and electron affinity of the system considered, we could apply this approach for photo chemical catalyst or the surface science.

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